

COMPREHENSIVE STRUCTURAL STUDY OF PRE- AND POST-HEAT TREATED COMPRESSION MOLDED POLYURETHANE SAMPLES OF VARYING COMPOSITION STUDIED BY SCANNING PROBE TECHNIQUES

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ABSTRACT

Only a limited number of structural studies have been performed on polyurethanes using scanning probe techniques to determine both the microstructure and the corresponding distribution of hard and soft segments within samples. This type of information is needed to better understand the mechanical properties of these materials and to facilitate modeling. In order to address these issues, we have fabricated a series of compression molded segmented poly(ester urethane) samples with hard (HS) to soft segment ratios from 19 to 100%. Samples were examined using scanning probe phase imaging techniques to obtain the topography and corresponding distribution of hard domains before and after heating at 100°C.

A number of significant differences were observed between the pre- and post-heat treated samples. Variations in structure and heat-induced morphological changes were directly related to HS content. Fine strand- or fibril-like structures were most prominent in the 23 and 19% HS sample but first appeared at 30% HS. Harder, thicker elongated structures dominated the surface of the 100% HS sample and were seen to a limited extent on all samples, especially after annealing and quenching. The 23% HS sample surface structure depended on quenching rate and time after treatment.

INTRODUCTION

Thermoplastic polyurethanes derive their elastomeric properties from the thermodynamic incompatibility of low glass transition temperature (T_g) soft segments (SS's) from covalently attached hard segments (HS's) (Fig. 1). The phase separation of the HS's into domains greatly increases the modulus and strength of the elastomer. Above 40°C, the polyurethane mechanical properties decrease rapidly with increasing temperature. This correlates with disruption of the hard domains (Fig. 1), which is complete above 80°C, where the elastomer becomes thermoplastic. Upon cooling to ambient temperatures, the hard segments are expected to phase separate and reform the network structure and the material once again is a tough elastomer. The recovery of the mechanical properties can take several days. While some general aspects of phase separation in segmented polyurethanes are known, details of the morphology and phase behavior of these complex materials are far from understood. Earlier studies primarily employed small angle x-ray and small-angle neutron scattering techniques to determine the morphology of these materials [1-4]. These studies indicated that at the higher HS densities the structures have characteristic length scales of the order of 10 nm.

Recently, scanning force microscopy (SFM) tapping modeTM techniques have begun to play an increasingly important role in determining structure over nanometer length scales in polymeric materials [6-9]. The cantilever oscillation frequency is sensitive to differences in interactions due to materials differences across the sample surface. One can use a combination of tapping mode and phase imaging techniques to get correlated information relating topography to

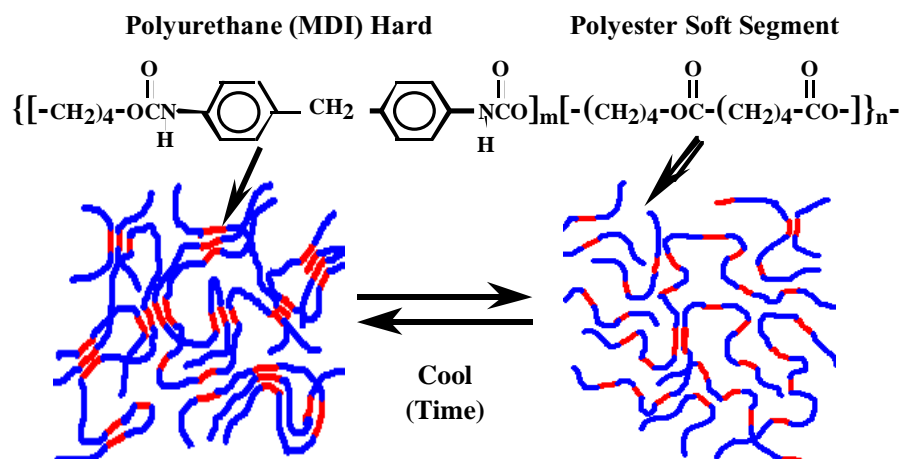


Figure 1. Poly(ester urethane segmented polymer structure [5].

“material’s information”, where material’s property variations are reflected in different phase shifts. In this study, the property of interest is relative hardness. The sensitivity of cantilever oscillation to relative hardness results in a nanophase distribution map based on hardness. In particular, phase imaging has been shown to give high resolution maps of HS and SS domains, providing invaluable local information about size, shape, and connectivity of domains. The SFM data can be used to understand structural changes due to heating and quenching samples and correlated with Differential Scanning Calorimetry (DSC) data. In this paper we have attempted to understand structure and HD distribution as a function of HS content. Further, we have begun preliminary studies to determine the effect of thermal history, both heating and cooling temperatures, times, and rates, on the HS domain structures for a wide range of HS content.

EXPERIMENTAL

In the present work we focus on poly(ester urethanes) containing 4,4’-methylene di(p-phenyl isocyanate) (MDI) + 1,4 butanediol (BDO) in the HS and poly(butylene adipate) in the SS. HS content is defined as

$$\%HS(wt) = \frac{wt\ MDI + wtBDO}{wt\ MDI + wtBDO + wtSS} \quad (1)$$

Samples were fabricated with different percentages of HS, as defined in Eq. 1, using MDI, BDO, dimethyl formamide (DMF) (Fisher Chemical Company) and poly(butylene adipate) oligomer (Rucoflex S101, Ruco Chemical Company). Prior to use the BDO and DMF were dried over calcium hydride overnight and then vacuum distilled. The MDI was recrystallized from hexane. The BDO and Rucoflex were heated in DMF at 100°C while the MDI in DMF was added. The resulting mixture was heated to 120°C (using an oil bath) for about 3 hours, after which time the solution became viscous. The solution was cooled to 55°C, and n-propanol was added to end cap the isocyanate. The polymer was precipitated by pouring the solution into water while agitating. The polymer was washed with water and methanol. The polymer was then dried in an oven at 60°C overnight. The samples, containing 19 (110°C), 23 (180°C), 30 (180°C), 36 (220°C), 57 (220°C), and 100 (180°C) wt % HS, were compression molded between teflon sheets at the temperatures indicated in parentheses. DSC is used to measure thermal properties associated with the disassociation of domain structure of poly(ester urethanes) (Fig. 1).

Surface structures were characterized with Nanoscope IIIa SFM’s using multimode and D3000 probes and 125 µm silicon cantilevers. Tapping mode and phase imaging techniques [9] were used to characterize the microstructure and HS distribution of samples before and after

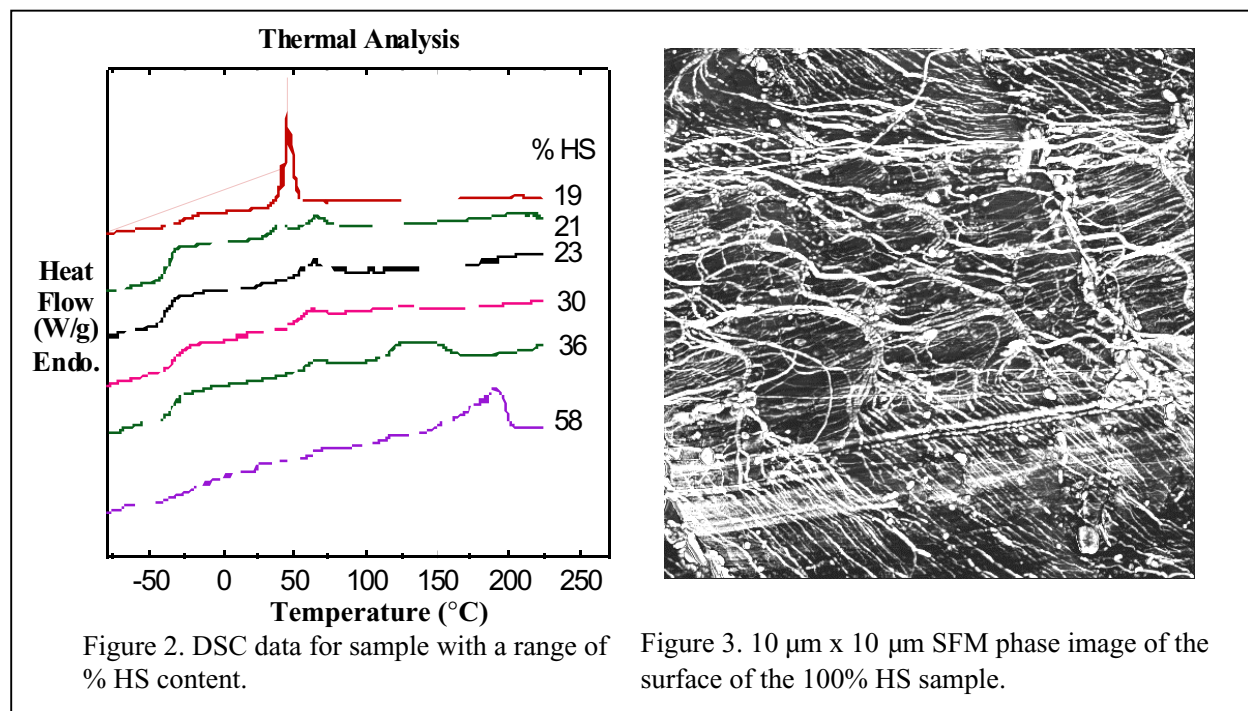
heating. Samples were imaged, heated at 100°C (10 minutes), quenched, and then reimaged. Moderate cantilever driving forces were used to ensure phase contrast but avoid contrast due to the mounting puck. Only the top surface of the sample was imaged in the present study. The 19, 23, 30, 36, and 57% HS samples were quenched on a pre-chilled Al block. The 23% HS sample was also quenched at room temperature to determine the effect of quenching rate on structure.°

RESULTS AND CONCLUSIONS

The DSC of samples with up to 39% HS shows a glass transition (T_g), which increases from -29° C at 19% HS to -22° C at 39% HS. The T_g is associated with the soft domains. In the 19% HS sample there is also a distinct endotherm at 40° C associated with SS melting. At higher HS densities there is a broad endotherm between 30° and 80° C (Fig. 2) associated with disruption of the hard domain network structure (Fig. 1). Endotherms at higher temperatures in the greater than 30% HS suggest the presence of HS domains in these samples that will be thermally stable at the 100C annealing temperature.

All samples were opaque before heating. The 100% HS sample was both brittle and slightly yellow. Optically, with the exception of the 100% HS sample, the surfaces were imprinted with the teflon surface structure, a result of the extrusion process in which the teflon sheets are produced. Upon heating at 100°C, the imprint structure and opacity persisted for samples with HS ≥ 30% HS. In contrast, both the 19 and 23% HS samples lost the teflon imprint and became clear and extremely smooth (~ a few tenths of a nm RMS roughness). All but the 100% HS sample shrank laterally on heating, with the largest dimensional change observed for low % HS samples. This shrinkage was accompanied by considerable thickening of the samples, suggesting the presence residual stress from the compression molding.

The changes in physical structure after heating as a function of HS content correlate with thermal data (Fig. 2): the most dramatic structural changes took place in the samples containing 23 or less % HS, with smaller changes seen for the samples with 30, 36, and 57% HS, and no change was observed on heating the 100% HS sample.



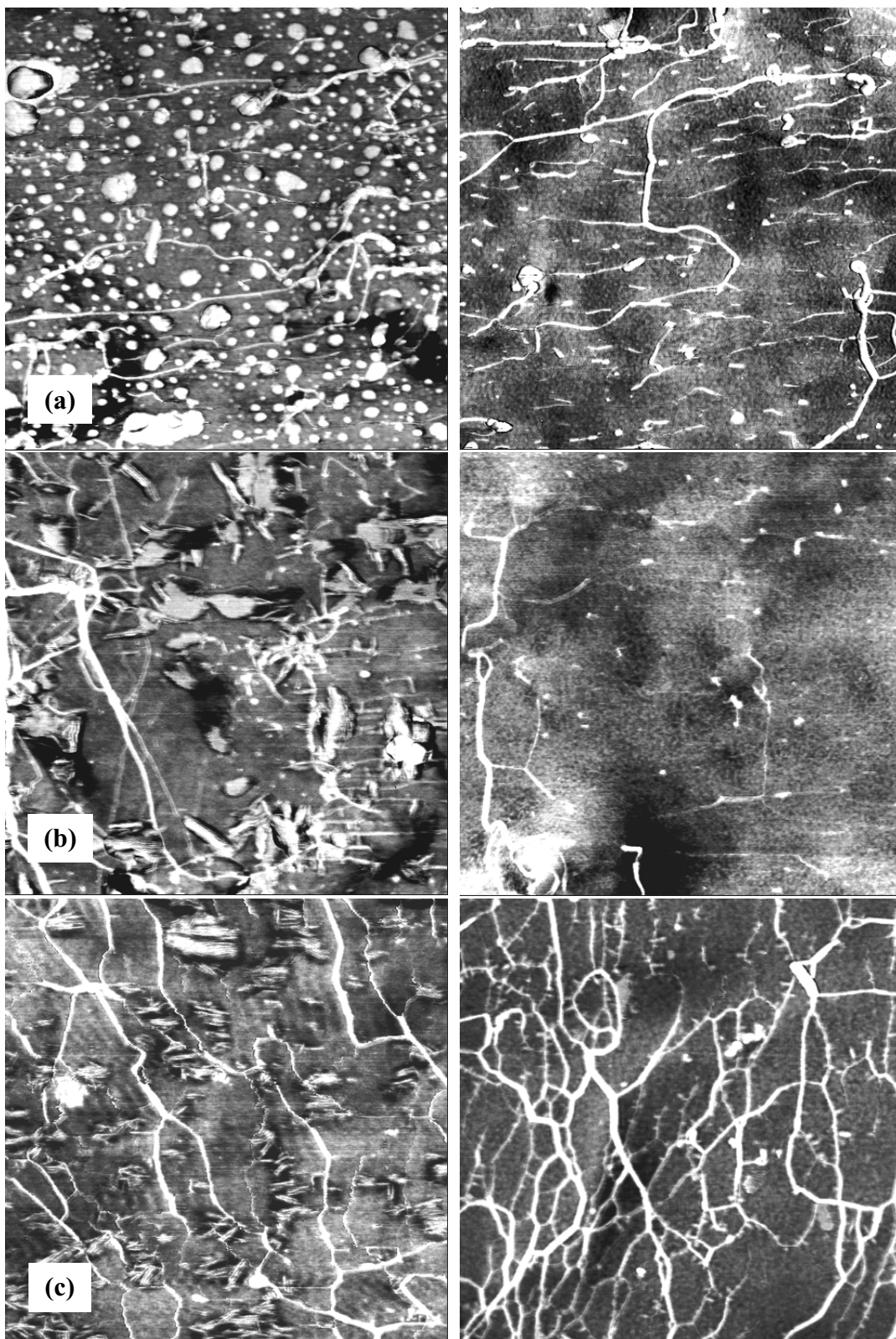


Figure 4. Composition of 2.5 μm x 2.5 μm SFM phase images of the surface of poly(ester urethane)samples before (column 1) and after heating at 100°C for 10 minutes (column 2): (a) 57% HS, (b) 36% HS, and (c) 30% HS.

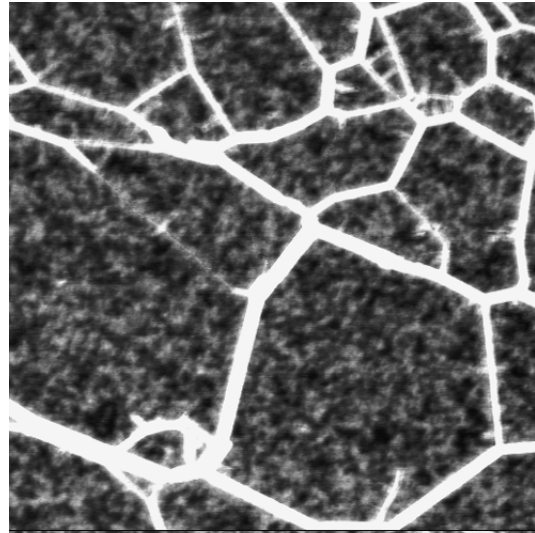
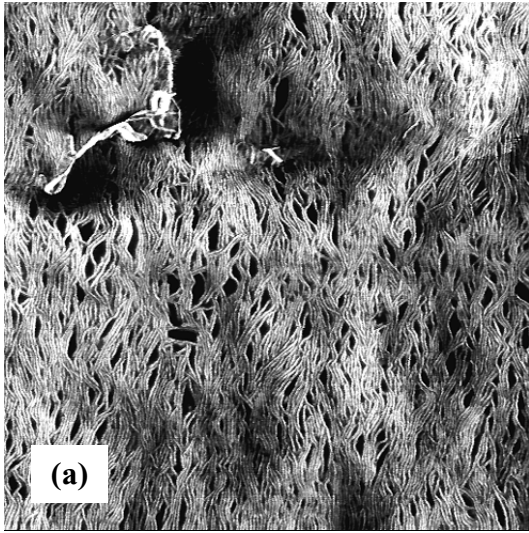


Figure 5. Composition of SFM 2.5 μm x 2.5 μm phase images of the surface of poly (ester urethane) samples before (column 1) and after heating at 100°C for 10 minutes (column 2): (a) 23% HS, (b) 23% HS 12 hrs after heating, and (c) 19% HS. Note: the surface of both of these samples were covered by ~10 nm diameter strands.

(b)

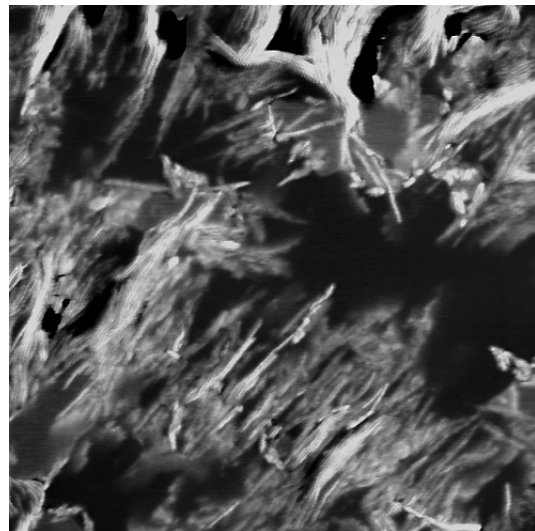
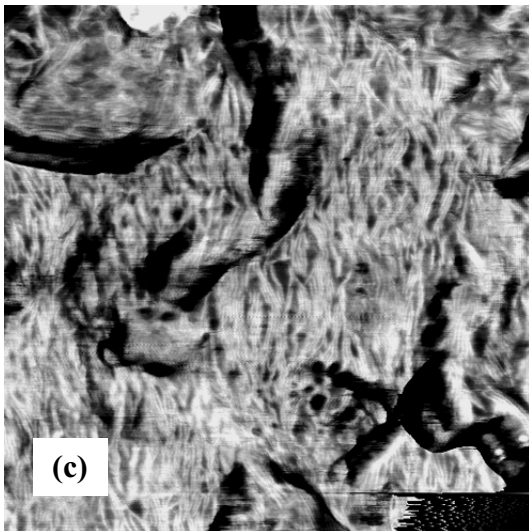
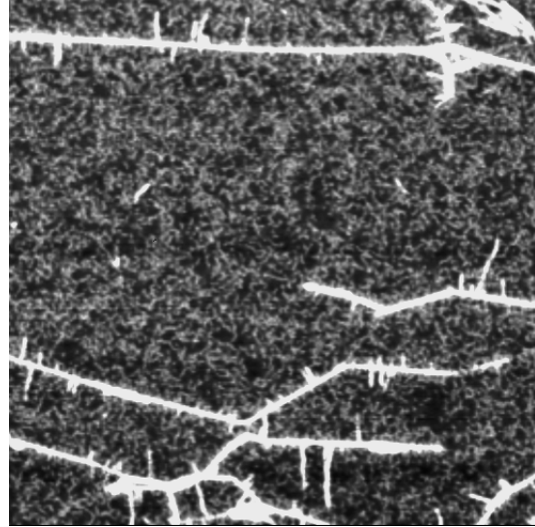


Fig. 3 shows a phase image of the surface of the 100% HS sample which is covered with long (5 to $> 20\ \mu\text{m}$, 20 - 80 nm thick) hard, parallel strands (often intertwined) oriented predominately in two directions ~ 60 degrees with respect to each other. The thickest strands appear to be bundles of thinner strands. Annealing had no obvious effect on the structure.

In contrast, the 30, 36, and 57% HS samples show fewer long hard strands (5-10 μm long, 10 to 20 nm wide) on the surface (Fig. 4). The 57% HS sample surface was covered with 20 to 80 nm round blobs before heating that were replaced by small square to rectangular structures about 15 - 20 nm wide and 30 - 75 nm long after heating. The smaller features on the surface of the 36 and 30% HS samples (more so on the latter) are actually aggregates of small strands (~ 10 nm wide). Some changes occurred after heating. The dominant surface structure brought out by heating on all three samples was a continuous softer matrix containing 10 to 20 nm wide, often convoluted, short cylinders of a harder phase. Unexpected, however, was a large interconnected crystalline network of a hard phase on the surface of the quenched 30% HS sample with shorter strands protruding from the longer ones at approximately 90° , possible due to the rapid quench.

Fig. 5 includes comparable images for the 23 and 19% HS samples. Prior to heating, both surfaces consisted of approximately parallel arrays of interconnected 10 nm thick strands. Whether this structure, seen previously on a cryo-microtomed compression molded sample, is localized at the surface is not yet known. After heating and quenching, three structural changes are obvious: 1) the strands disappeared, the annealing-quenching process resulted in a similar network of interconnected crystalline hard phase material with smaller, 90° branches, as in the 30% HS sample, and 3) the surface is again dominated by a soft matrix with imbedded hard phase material. Two interesting differences were seen in the 23% HS sample. The sample in Fig. 5a was quenched on a room temperature block. A sample quenched on a chilled block ended with in a surface completely covered by a fractal-like network of long large hard phase strands with 90° branches of smaller strands forming hillocks filling the gaps. The phase image taken 12 hrs after heating (Fig. 5b) shows considerable growth of the side branches and a more well defined HS-SS nanophase segregation with the HS phase width narrowed from 20 to 10 nm.

We found no clear evidence for lamellar structure assumed in the analysis of small-angle scattering data [2] in the phase images of any of our samples. The 5 to 20 nm wide HS domains in a SS matrix structure is consistent with observation of others in the range of % HS seen here [6-8] and with the sizes of the structures observed in the scattering measurements [1-4,8]. We believe this is the first observation of 10 nm wide parallel strands covering significant areas of 23 and 19% HS materials and, as well as, direct observation of time-dependent post-heating structural evolution.

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